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Second-Order Perturbation Theory in Atomic and Molecular Quantum Mechanics (Application to the Electric Dipole and Quadrupole Polarizabilities and Shielding Factors of the Beryllium Atom)

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Second-Order Perturbation Theory in Atomic and Molecular Quantum Mechanics (Application to the Electric Dipole and Quadrupole Polarizabilities and Shielding Factors of the Beryllium Atom)

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A new method, previously used in calculating atomic correlation energies, is shown to be applicable to a wide variety of atomic and molecular problems. Use is made of the fact that it is possible in many problems to calculate exactly the first-order perturbation correction to uncoupled Hartree–Fock wavefunctions and also second-order energy expressions. Particular application is made to the numerical calculation of dipole and quadrupole polarizabilities and shielding factors for the beryllium atom.

I. INTRODUCTION

THE subject of weak interactions (perturbations) in atomic and molecular problems has been treated in many papers in the last decade.[1,2] Because of their small magnitude these perturbations are usually ignored in the determination of electronic wavefunctions. To obtain such small contributions by differences in two variational calculations, one with and one without the added terms, the variational calculations would have to be done to as yet unachieved numerical accuracy. Perturbation theory is ideally suited for such calculations because the perturbations are truly small and because it avoids loss of numerical accuracy by calculating these quantities directly.

In Sec. II we discuss the methods of solution of the perturbation problem and the new method of exact solution of the first-order perturbation wavefunction and, hence, the second-order energy for the uncoupled Hartree–Fock model. This method, previously used in calculating the correlation energy of the beryllium atom,[3] utilizes a complete set of single-particle Hartree–Fock states. This basis set has the surprising property that it contains the Hartree–Fock orbitals of the ground state and all other orbitals are in the continuum for most neutral atoms and molecules. The basis set is discussed in Sec. III. In Sec. IV this method is applied to a calculation of the electric dipole and quadrupole polarizabilities and shielding factors of the beryllium atom.

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[1] Review articles: (a) M. Karplus, Rev. Mod. Phys. **32**, 455 (1960). (b) A. Dalgarno, Advan. Phys. **11**, 281 (1962). (c) P. Cade, "*The Theoretical Calculation of the Properties of Molecules,*" University of Wisconsin Report, WIS–AEC–21, 18 May 1959. This report contains a complete survey of the literature prior to 1959. In this paper the term "weak interactions" refers to small perturbations and not to the weak interactions of nuclear physics.
[2] M. Karplus, J. Chem. Phys. **37**, 2723 (1962).
[3] H. P. Kelly, Phys. Rev. **131**, 684 (1963).

Any second-order problem discussed in Refs. 1, e.g., NMR shielding constants, paramagnetic susceptibilities, time-dependent electric and magnetic susceptibilities, etc., can be handled by the method of this paper.

II. PERTURBATION METHODS

The problem to be solved is[4]

$$(H_0 + \lambda H_1 - E) U = 0, \qquad (1)$$

where H_0 and H_1 are any two Hermitian operators and λ is a smallness parameter. The eigenfunction U and the eigenvalue E are expanded in powers of this parameter:

$$E = \sum_{n=0}^{\infty} \lambda^n E_n,$$

$$U = \sum_{n=0}^{\infty} \lambda^n U_n. \qquad (2)$$

When these expansions are substituted into Eq. (1), an infinite set of coupled equations is obtained; the first two are

$$H_0 U_0 - E_0 U_0 = 0, \qquad (3)$$

$$(H_1 - E_1) U_0 = (E_0 - H_0) U_1, \qquad (4)$$

where

$$E_1 = \int U_0 H_1 U_0 d\tau, \qquad (5)$$

$$E_2 = \int U_0 H_1 U_1 d\tau, \qquad (6)$$

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[4] The formulation given in this section is that presented by H. A. Bethe and E. E. Salpeter in *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), Sec. 25.

written and used to solve for $P_{kl}(r)$. Another possibility is to use Hartree's numerical methods.[12] Asymptotically, $P_{kl}(r)$ should approach $A\sin[kr+\delta_l-l(\pi/2)]$. Once the integrodifferential equation (14) or (15) has been solved, the phase shift δ_l may be readily obtained. If the normalization $A=1$ is used, then $\sum_k$ may be replaced by

$$\sum_{l,m_l,m_s}\left(\frac{2}{\pi}\right)\int_0^\infty dk.$$

(See Ref. 3, Sec. 4C for proof.) In solving Eq. (15) it is necessary to consider integrals of the form

$$\int_r^\infty dr P_{kl}(r)\frac{1}{r^{K+1}}P_{n_jl_j}(r)$$

in the exchange term. It was found convenient in the numerical work of Ref. 3 to replace the above integral by

$$\left(\int_0^\infty dr-\int_0^r dr\right)P_{kl}(r)\frac{1}{r^{K+1}}P_{n_jl_j}(r).$$

The only quantity which has to be estimated, then, in each iteration of Eq. (15) is

$$\int_0^\infty dr P_{kl}(r)\frac{1}{r^{K+1}}P_{n_jl_j}(r).$$

For molecules, because of the lack of spherical symmetry, the variables of the Hartree–Fock equations cannot be separated and the equation cannot be numerically integrated. In such cases LCAO fits can be obtained for the continuum states. In this paper only the Be atom has been treated. In future publications, calculations will be made for molecules. In any
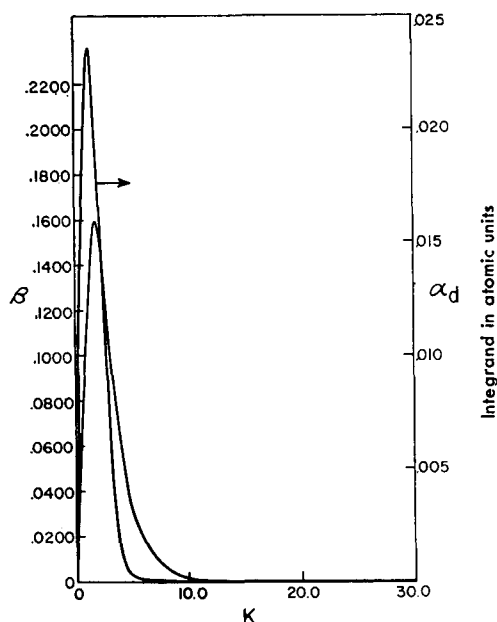

FIG. 2. The $2s$ contributions to integrands of α_d and β. See Eqs. (18) and (19).

case, it is expected that no intrinsic difficulties occur in using this method for molecules.

IV. POLARIZABILITIES AND SHIELDING FACTORS

In this section, using the beryllium numerical Hartree–Fock radial functions P_{1s} and P_{2s} of Kibartas and Yutsis,[13] the dipole and quadrupole polarizabilities and shielding factors are calculated for Be. For a full discussion of these quantities see Ref. 1(b). This problem was chosen because it is one of the few problems that has been solved by numerical integration of Eq. (4).[5] Since direct integration is equivalent to use of Eq. (8), the ideas of this method can be verified by comparing the answers obtained by the two methods. The purpose of this section is not to produce any new results but to demonstrate the use of a new method of calculation. It should be noted that this method can be applied to all second-order problems. For example, in the calculations of this section, the numerical functions $P_{kl}(r)$ which had been tabulated on IBM cards for the correlation energy calculation of Ref. 3 were used directly. In order to improve the mesh size for the numerical integration it was necessary to calculate a few additional $P_{kl}(r)$.

According to Dalgarno,[1b] the 2^L-pole polarizability is given by

$$\alpha_{2^L}=2[U_1^{(L)},\sum_{i=1}^N r_i^L P_L(\cos\theta_i)U_0]; \qquad (16)$$

$U_1^{(L)}$ is the first-order correction to the wavefunction U_0 due to the perturbation

$$-\sum_{i=1}^N r_i^L P_L(\cos\theta_i).$$

The 2^L-pole shielding factor is given by

$$\gamma_{2^L}=2\left[U_1^{(L)},\sum_{i=1}^N\frac{P_L(\cos\theta_i)}{r_i^{L+1}}U_0\right]. \qquad (17)$$

FIG. 1. The $1s$ contributions to the integrands of α_d and β. See Eqs. (18) and (19).

[12] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), Chap. 4, Sec. 4.5, and Chap. 5, Sec. 5.2.1.
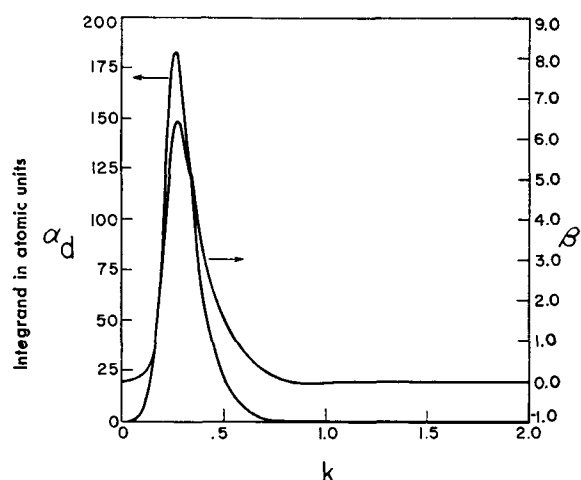
[13] V. V. Kibartas and A. P. Yutsis, Zh. Eksperim. i Teor. Fiz. **25**, 264 (1953).

The dipole and quadrupole polarizabilities and shielding factors are now expressed in terms of the single-particle orbitals, using the notation of this paper. All angular integrations have been performed and atomic units are used.[12]

$$\text{Dipole polarizability} = \alpha_d = \frac{8}{3\pi} \left[\int_0^\infty dk \, \frac{\left| \int_0^\infty dr P_{1s}(r) r P_{k1}(r) \right|^2}{k^2/2 - \epsilon_{1s}} + \int_0^\infty dk \, \frac{\left| \int_0^\infty dr P_{2s}(r) r P_{k1}(r) \right|^2}{k^2/2 - \epsilon_{2s}} \right] \quad (18)$$

$$\text{Dipole shielding} = \beta_\infty = \frac{8}{3\pi} \left\{ \int_0^\infty dk \frac{\left[\int_0^\infty dr P_{1s}(r) r P_{k1}(r) \right] \left[\int_0^\infty dr P_{1s}(r) 1/r^2 P_{k1}(r) \right]}{k^2/2 - \epsilon_{1s}} \right.$$

$$\left. + \int_0^\infty dk \frac{\left[\int_0^\infty dr P_{2s}(r) r P_{k1}(r) \right] \left[\int_0^\infty dr P_{2s}(r) 1/r^2 P_{k1}(r) \right]}{k^2/2 - \epsilon_{2s}} \right\} \quad (19)$$

$$\text{Quadrupole polarizability} = \alpha_q = \frac{8}{5\pi} \left[\int_0^\infty dk \, \frac{\left| \int_0^\infty dr P_{1s} r^2 P_{k2}(r) \right|^2}{k^2/2 - \epsilon_{2s}} + \int_0^\infty dk \, \frac{\left| \int_0^\infty dr P_{2s}(r) r^2 P_{k2}(r) \right|^2}{k^2/2 - \epsilon_{2s}} \right] \quad (20)$$

$$\text{Quadrupole shielding} = \gamma_\infty = \frac{8}{5\pi} \left\{ \int_0^\infty dk \frac{\left[\int_0^\infty dr P_{1s}(r) r^2 P_{k2}(r) \right] \left[\int_0^\infty dr P_{1s}(r) 1/r^3 P_{k2}(r) \right]}{k^2/2 - \epsilon_{1s}} \right.$$

$$\left. + \int_0^\infty dk \frac{\left[\int_0^\infty dr P_{2s}(r) r^2 P_{k2}(r) \right] \left[\int_0^\infty dr P_{2s}(r) 1/r^3 P_{k2}(r) \right]}{k^2/2 - \epsilon_{2s}} \right\} . \quad (21)$$

In order to calculate the quantities in Eqs. (18)–(21), a number of $P_{kl}(r)$ used in the correlation energy calculation[3] were used to calculate matrix elements such as

$$\int_0^\infty dr P_{2s}(r) r P_{k1}(r) .$$

The variation with k was studied and additional $P_{k1}(r)$ and matrix elements were calculated until a smooth variation with k was obtained. At this point the numerical integration over k was performed. All integrations described were performed by Simpson's rule. At the outset of any given calculation it is difficult to predict which values of k will be important. However, in this calculation and a previous one[3] this presented no serious obstacles.

As an example, Tables I and II and Figs. 1 and 2 contain values and graphs of the integrands of Eqs.

(18) to (21). Table III gives the results of this calculation. The values for the dipole polarizability and shielding factor and also for the quadrupole polarizability are in excellent agreement with those reported by Dalgarno and McNamee.[5] Our value for the quadrupole shielding factor, 0.671, is only in fair agreement with the value 0.77 reported by Dalgarno and McNamee. Although our calculation of γ_∞ is the least accurate of the four quantities reported, we do not feel that the numerical inaccuracy of this calculation is sufficient to account for the discrepancy. At present, the distance between the two results is unresolved. Dalgarno and McNamee give no indication of their accuracy nor details of their method in their paper. There are errors in this calculation, as in Dalgarno and McNamee's, due to the neglect of electron correlations in the zero-order functions. These errors tend to cause polarizabilities and shielding factors calculated in the Hartree–

TABLE I. The $P_{1s}(r)$ contributions to the integrands of Eqs. (18) and (19) in atomic units.

k	$\dfrac{\left\lvert\displaystyle\int_0^\infty P_{1s}(r)\,r\,P_{k1}(r)\,dr\right\rvert^2}{\epsilon_{1s}-k^2/2}$	$\dfrac{\left(\displaystyle\int_0^\infty P_{1s}(r)\,r\,P_{k1}(r)\,dr\right)\left(\displaystyle\int_0^\infty P_{1s}(r)\,r^{-2}P_{k1}(r)\,dr\right)}{\epsilon_{1s}-k^2/2}$
0.050	0.00000721	0.0000291
0.100	0.00014006	0.0005679
0.150	0.00096832	0.0039339
0.200	0.00424285	0.0175001
0.225	0.00737040	0.0301193
0.250	0.01080001	0.0442359
0.275	0.01331940	0.0546994
0.300	0.01450957	0.0597511
0.325	0.01476666	0.0609958
0.350	0.01460633	0.0605380
0.375	0.01433019	0.0596052
0.400	0.01410867	0.0589124
0.450	0.01396498	0.0588076
0.500	0.01414437	0.0617897
0.550	0.01459644	0.0627051
0.600	0.01526303	0.0663522
0.650	0.01605970	0.0706733
0.700	0.01695721	0.0756387
0.750	0.01788440	0.0809372
0.800	0.01882382	0.0865192
0.850	0.01977257	0.0923882
0.900	0.02066225	0.0982291
0.950	0.02150185	0.1041112
1.000	0.02226383	0.1098750
1.100	0.02350398	0.1208307
1.200	0.02433687	0.1307473
1.300	0.02473925	0.1393036
1.400	0.02473924	0.1464076
1.500	0.02456742	0.1519484
1.600	0.02368712	0.1559996
1.700	0.02275030	0.1585717
1.800	0.02162089	0.1597874
1.900	0.02035100	0.1597574
2.000	0.01899387	0.1586062
2.250	0.01548261	0.1516946
2.500	0.01217033	0.1407337
2.750	0.00931016	0.1275299
3.000	0.00698200	0.1135137
3.250	0.00516264	0.0996705
3.500	0.00378115	0.0866259
3.750	0.00275545	0.0747416
4.000	0.00199951	0.0641521
4.250	0.00145099	0.0548837
4.500	0.00105434	0.0468598
4.750	0.00076805	0.0399724
5.000	0.00056129	0.0340899
5.500	0.00029109	0.0243186
6.000	0.00016686	0.0181614
7.000	0.00005414	0.0099769
8.000	0.00001905	0.0056669
9.000	0.00000731	0.0035523
10.000	0.00000299	0.0020473
11.000	0.00000135	0.0013116
12.000	0.00000062	0.0008485
14.000	0.00000015	0.0003887
16.000	0.00000004	0.0001873
18.000	0.000000014	0.0000969
20.000	0.000000005	0.0000554
25.000	0.000000004	0.0000117
30.000	0.000000002	0.0000121
40.000	0	0
50.000	0	0

Fock model to be too large. The possibility exists of treating simultaneously the weak interaction and correlation perturbation; this will be the subject of future study. The only quantity calculated in this paper which is known exactly is the dipole shielding factor, β_∞. As discussed in Ref. 1(b), β_∞ can be shown to be 1.00 for all neutral atoms, as compared with the value 1.77 calculated in this paper.

TABLE II. The $P_{2s}(r)$ contributions to the integrands of Eqs. (18) and (19) in atomic units.

k	$\dfrac{\left\|\int_0^\infty P_{2s}(r)rP_{k1}(r)dr\right\|^2}{\epsilon_{2s}-k^2/2}$	$\dfrac{\left(\int_0^\infty P_{2s}(r)rP_{k1}(r)dr\right)\left(\int_0^\infty P_{2s}(r)r^{-2}P_{k1}(r)dr\right)}{\epsilon_{2s}-k^2/2}$
0.025	0.01668946	0.00040352
0.05	0.27280593	0.00667548
0.075	1.43185423	0.03556810
0.10	4.7559999	0.12264762
0.125	12.3729559	0.32362105
0.15	27.5078705	0.74519897
0.175	54.17801142	1.52891609
0.200	93.81137032	2.78213743
0.2125	118.06179406	3.58260733
0.225	141.44609631	4.40961588
0.2375	161.70724968	5.18773844
0.25	176.13279418	5.82106844
0.2625	182.76662496	6.23111280
0.275	181.92928654	6.40699503
0.2875	174.83209470	6.36955408
0.30	163.54402635	6.16969893
0.325	135.45477300	5.50119809
0.35	107.49872369	4.72390058
0.375	83.38712403	3.98648411
0.400	64.02456264	3.34632079
0.425	49.02772812	2.81185997
0.45	37.17497089	2.35351738
0.475	27.87532596	1.96045588
0.500	20.76357042	1.63088548
0.55	11.03007266	1.10515589
0.60	5.46434841	0.72352200
0.65	2.73602211	0.47464813
0.70	0.879175052	0.24832027
0.725	0.46406394	0.17278178
0.75	0.21066890	0.11133724
0.775	0.06994683	0.06120580
0.800	0.00888660	0.02076033
0.825	0.00231083	−0.01005833
0.85	0.02946623	−0.03400750
0.875	0.07682700	−0.05184196
0.90	0.13400083	−0.06440500
0.95	0.2492597	−0.07686653
1.0	0.34213768	−0.07741929
1.1	0.43077981	−0.05934279
1.2	0.41852943	−0.03297240
1.3	0.36097785	−0.00867071
1.4	0.29001554	+0.01018638
1.5	0.22394331	0.02324213
1.6	0.16817053	0.03126413
1.7	0.12450798	0.03545717
1.8	0.09129697	0.03688086
1.9	0.06723696	0.03663025
2.0	0.04929644	0.03514126
2.25	0.02269741	0.02903467
2.50	0.01123554	0.02311136
2.75	0.00555678	0.01763100
3.0	0.00303166	0.01376034
3.25	0.00161051	0.01041313
3.50	0.00094307	0.00817928
3.75	0.00054573	0.00632103

TABLE II (*Continued*)

k	$\dfrac{\left\| \int_0^\infty P_{2s}(r)rP_{k1}(r)\,dr \right\|^2}{\epsilon_{2s}-k^2/2}$	$\dfrac{\left(\int_0^\infty P_{2s}(r)rP_{k1}(r)\,dr\right)\left(\int_0^\infty P_{2s}(r)r^{-2}P_{k1}(r)\,dr\right)}{\epsilon_{2s}-k^2/2}$
4.00	0.00032778	0.00494827
4.25	0.00020113	0.00389655
4.50	0.00012822	0.00311562
4.75	0.00008485	0.00253069
5.00	0.00005667	0.00206050
5.50	0.00002469	0.00134291
6.00	0.00001197	0.00091908
7.00	0.00000307	0.00044606
8.00	0.00000109	0.00025300
9.00	0.00000033	0.00013310
10.0	0.00000012	0.00007626
11.0	0.00000006	0.00005137
12.0	0.00000002	0.00002973
14.0	0	0.00001269
16.0	0	0.00000638
18.0	0	0.00000583
20.0	0	0.00000250
25.0	0	0.00000461
30.0	0.00000001	0.00000997

CONCLUSIONS

It has been shown in this paper that quantities involving weak perturbations may be calculated to second order in perturbation theory with a Hartree–Fock ground-state approximating the true initial unperturbed state. The method described necessitates obtaining a complete set of single-particle Hartree–Fock states and it was shown that for most neutral atoms and molecules the unoccupied states are then readily replaced by integrations. This method has the advantage that once the complete set of single-particle states has been calculated, all second-order quantities can be calculated with little extra work. The Introduction of this paper indicated the many different types of problems that can be treated and in Refs. 1a, 1b, and 1c many other second-order problems are discussed. Higher-order perturbations can of course be calculated but the work becomes more difficult (though not always prohibitive, e.g., see Ref. 3). However, it should be noted that in this perturbation calculation, which corresponds to the uncoupled Hartree–Fock approximation used by Dalgarno,[1b] the dipole shielding factor is 1.77 compared to the theoretical value of 1.00. This indicates that higher-order terms in the expansion must be considered before truly accurate results can be obtained. As it stands, the method of this paper is applicable to any problem for which any of the various forms of perturbation theory rapidly converge and for which the Hartree–Fock is a good zero-order approximation.

TABLE III. Results of the calculation.

	$\alpha_d (A^0)^3$	β	$\alpha_q (A^0)^5$	γ_∞
1s contribution	0.0068	0.455	0.00057	0.163
2s contribution	4.537	1.316	9.255	0.508
Total	4.54	1.77	9.26	0.671
Dalgarno–McNamee	4.5	1.8	9.1	0.77